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(71) Applicant
Fuji Photo Film Co. Ltd.

(Incorporated in Japan)

**210 Nakanuma, Minamiashigara-shi,
Kanagawa 250-01, Japan**

(72) Inventors
**Jun Sasaki
Kyoichi Naruo**

(74) Agent and/or Address for Service
**Gee & Co.
Chancery House, Chancery Lane, London, WC2A 1QU**

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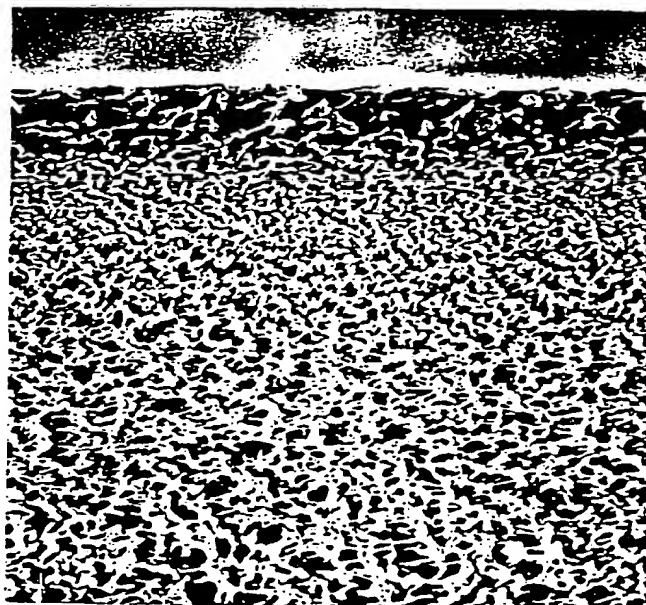
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**B5B
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B01D**

(54) **Polymeric micro-porous membranes and their production**

(57) The membrane has a distribution of pore diameters in the direction of its thickness (ie asymmetric) and contains a layer of pores of minimum size inside the membrane, preferably 1-30 μ below the surface. It is produced by (a) preparing a polymer solution using a good solvent for the polymer and optionally a non-solvent for the polymer; (b) spreading the solution over a support; (c) causing a phase separation on the surface to obtain the inside layer of minimum pore size and (d) immersing the membrane in a solidifying liquid. At (c), preferably air having an absolute humidity above 2g H₂O/Kg is blown onto the surface at a rate above 0.2m/sec. The membrane is useful for filtration of particles from a liquid at good flow rates.

FIG. 1



X2000

P.O.
ORIGINAL

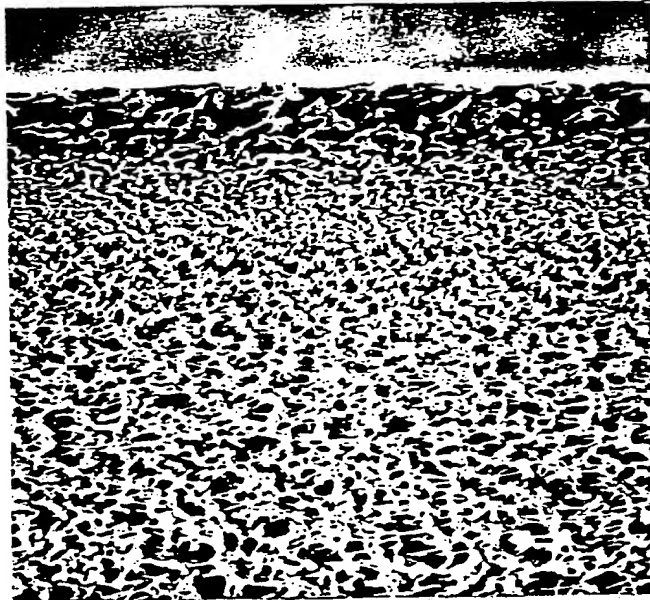
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FIG. 1

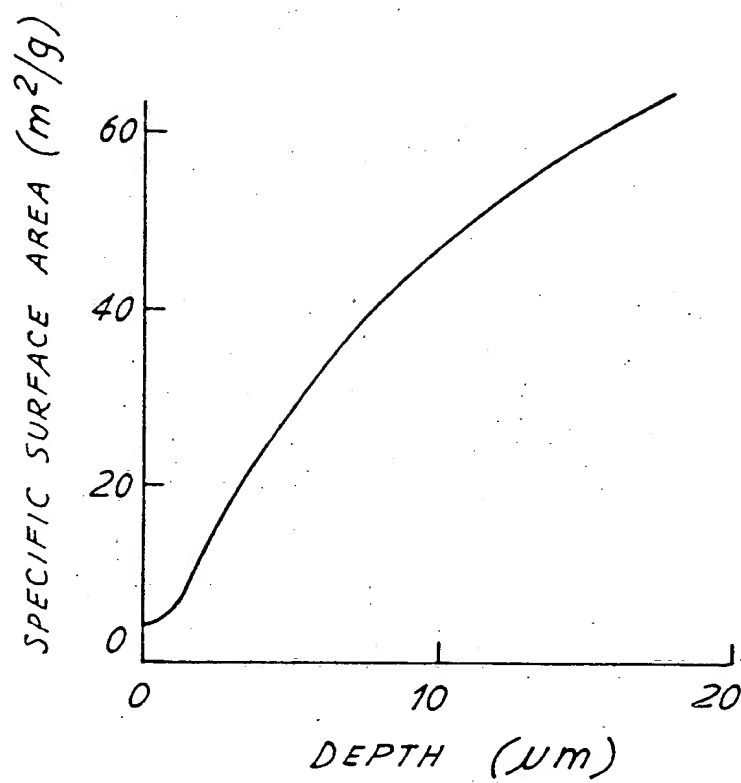


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FIG. 2



POLYMERIC MICRO-POROUS MEMBRANES
AND THEIR PRODUCTION

The present invention relates to asymmetric micro-porous membranes. More particularly, it relates to micro-porous membranes having a good filtration efficiency.

Micro-porous membrane have been known for quite a long time (see e.g. "Synthetic Polymeric Membranes" by R. Kesting published by McGraw Hill Co.) and widely used for filtration, etc. They are produced by using cellulose esters as starting materials as described in U.S. Patents Nos. 1,421,341, 3,133,132 & 2,944,017, and Japanese Patent Publications Nos. 15,698/'68, 33,313/'70, 39,586/'73 & 40,050/'73, by using aliphatic polyamides as described in U.S. Patents Nos. 2,783,894, 3,408,315, 4,340,479, 4,340,480 & 4,450,126, German Patent No. 3,138,525, and Japanese Patent Publication (OPI) No. 37,842/'83 (the term "OPI" as used herein means an un-examined published application), by using polyfluorocarbons as disclosed in U.S. Patents Nos. 4,196,070, & 4,340,482, and Japanese Patent Publications (OPI) Nos. 99,934/'80 & 91,732/'83, by using polysulfones as shown in Japanese Patent Publications (OPI) Nos. 154,051/'81, 86,941/'81 & 12,640/'81, and employing polypropylene as shown in German Patent OLS 3,003,400. These micro-porous membranes are used for, e.g., filtering or sterilizing cleaning water for the electronic industry, water for pharmaceuticals including that used in their manufacturing processes, water for foodstuffs, etc. The uses of the membrane and the amount thereof consumed have increased recently. In particular highly reliable micro-porous membranes are much used for the purpose.

of catching fine particles.

Such micro-porous membranes are divided of two types, i.e., (1) the so-called symmetric membrane: the micro-pores in this membrane have diameters which substantially do not vary in the direction of its thickness and those on both sides of its have substantially the same diameter, and (2) the so-called asymmetric membrane: its micro-pores have diameters which vary continuously or discontinuously in the direction of its thickness and the diameters of those on one side of the membrane differ from those on the other side of it.

The symmetric membrane, as explained in Japanese Patent Publication No. 5,793/'79 and Japanese Patent Publication (OPI) No. 99,303/'83 (corresponding to European Patent No. 50,789), gives a great resistance to the flow of a fluid on its filtration so that the flow rate is low (that is, only a low flow rate is obtainable per unit area, unit period of time and unit pressure difference). Also, the filtration ability of the membrane can not last long since its pores tend to be blocked easily, i.e., no anti-blocking ability.

On the other hand, the asymmetric membrane, as described in Japanese Patent Publication No. 6,406/'80 or OPI No. 154,051/'81 (corresponding to European Patent No. 36,315), has on its surface a fine layer which contains pores of the shortest diameters, whereby fine particles of a minimum size can be substantially caught and removed here on filtration. This means that all the thickness of the membrane can be efficiently utilized as a filter so that it is possible to increase the filtration flow rate as well as to prolong the life of the membrane as a filter, when it is used with care.

In the above case, however, since the fine layer which is very important is on the surface of the membrane,

it tended to get scratched or abraded, often resulting in an escape of fine particles.

To solve this problem, the fine layer having micro-pores of the shortest diameters is desired to be
5 inside a membrane for filtration. For example, Japanese Patent Publication (OPI) No. 150,402/'83 (corresponding to European Patent No. 83,489) proposed a structure in which two asymmetric membranes were adjusted together in layers in such a manner as their fine layer's sides come in contact.
10 However, in such a filter of layered asymmetric membranes, when it is folded in an accordion fold and placed in a cartridge, the filtration area within the cartridge becomes small and therefore, the filtration flow rate as a module gets low. Accordingly, it has been strongly desired in this
15 industry to invent a structure which has said fine layer inside a single membrane.

In order to overcome the above problem, the present inventors studied in detail one of the traditional methods for producing micro-porous membranes, i.e., a dry-
20 wet method, in which a polymer solution is spread and allowed to stand in air for a certain period of time to cause a micro-phase separation whereby the diameter of the micro-pores is controlled. Such method was divided into two types, e.g., the one is a method to let the solvent used
25 evaporate thoroughly (e.g., Japanese Patent Publication (OPI) No. 102,416/'80) and the other is a method in which the spread polymer solution is hardly left to let the solvent evaporate and is immersed in a solidifying bath (e.g., Japanese Patent Publications (OPI) Nos. 8,887/'80 & 154,051/
30 '81).

In contrast to these two methods, the present inventors discovered that, surprisingly enough, a layer of minimum pores can be formed at a certain depth inside a micro-porous membrane when evaporation of the solvent from the spread polymer solution is suitably controlled,

while a highly accurately adjusted amount of vapor of a non-solvent to the polymer is given to said spread solution from the air so as to let the solution absorb the vapor through its spread surface, whereby a micro-phase separation is caused to occur to a certain depth below the surface of the spread solution.

Further, the present inventors analyzed the mechanism of filtration and blocking of membranes as well as the relation between the specific surface area and the filtration life of membranes, and discovered that the following two points are important factors related to the filtration life:

(a) When the structure of a membrane is made extremely asymmetrical, its specific surface area gets small and the inlet side above the minimum pore layer does not effectively function as a pre-filter, and

(b) Particles are not necessarily trapped where the diameter of the pores are smaller than that of the particles and most of the particles are trapped by adhering to walls inside the membrane.

Therefore, the inventors found it rational not to make a membrane too asymmetrical so that the specific surface area of the membrane can be large enough to extend its filtration life. Our further study revealed that a membrane having a specific surface area of not less than $8 \text{ m}^2/\text{g}$ can be prepared by controlling the amounts of the solvent vapor and the non-solvent absorbed from the atmosphere in the process between spreading of a membrane forming solution and immersion of the spread solution in a solidifying liquid, and thereby life of the micro-porous membrane can be extended.

Thus, the first object of the present invention is to provide a micro-porous membrane which has a small filtration resistance and a high filtration flow rate.

The second object is to provide a micro-porous membrane of which filtration ability will not easily

deteriorate due to any damage on its surface.

The third object is to provide a micro-porous membrane which can catch fine particles and bacteria efficiently and has a long filtration life.

5 The above-mentioned objects of the present invention have been accomplished by a micro-porous membrane which is characterized by having a distribution of micro-pores diameters in the direction of the thickness and containing a layer of minimum pores inside the membrane
10 (hereinafter referred to as "both sides asymmetric membrane").

Since the micro-porous membrane of the present invention has a pore diameter distribution in the direction of its thickness, the whole body of the membrane can be effectively used as a filter. Accordingly, the filtration
15 flow rate can be increased and the life as a filter is prolonged. Moreover, as the layer of minimum pores exists not on the surface of the membrane but inside it, a risk of being damaged by scratches, etc. is minimized, which makes the membrane highly advantageous in its handling. Also, it
20 can be used as a cartridge type filter just like an ordinary micro-porous membrane consisting of one sheet.

In the accompanying drawing:

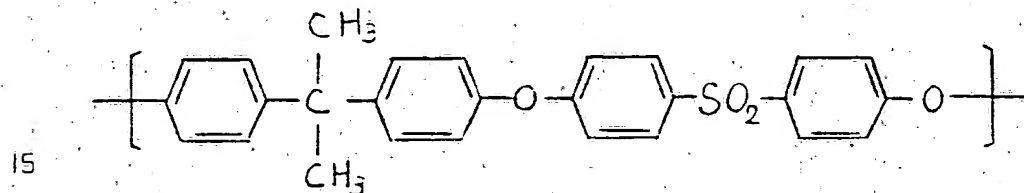
Figure 1 is an electron microscopic photograph at 2,000 magnification, which shows a section of the micro-
25 porous membrane obtained in Example 2 by blowing air for 4 seconds before immersing in a solidifying bath containing water at 20 °C.

Figure 2 is a graph obtained in Example 3, which shows the relation between the specific surface area and the
30 depth of the layer of minimum pores produced.

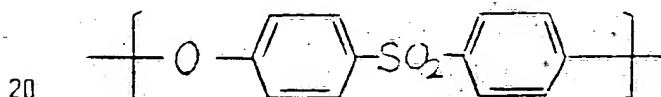
The polymer used for forming a membrane in this invention is not particularly restricted. It can be chosen depending on the uses of such asymmetric porous membranes or other purposes. Examples of such a polymer are

cellulose acetate, nitrocellulose, polysulfone, polyether sulfone, polyacrylonitrile, styrene-acrylonitrile copolymer, styrene-butadiene copolymer, saponified products of ethylene-vinyl acetate copolymer, polyvinyl alcohol, 5 polycarbonate, organosiloxane-polycarbonate copolymer, polyester carbonate, organopolysiloxane, polyphenyleneoxide, polyester, polyamide, polyimide, polyvinylidene fluoride, polyvinyl acetate, polyamideimide, polybenzimidazole.

Of these polymers, the polysulfone and/or 10 polyethersulfone are preferable and polymers having the following formula as a repeating unit are best.



or



The micro-porous membrane of the present invention is produced as follows: The above polymer is dissolved into 25 (1) a good solvent, (2) a mixture of a good solvent and a non-solvent, or (3) a mixture of more than one of the solvents which have different solubilities with one another, to prepare a raw solution for a membrane. Then, the solution is spread over a support and immersed in a 30 solidifying liquid to form a membrane, which is rinsed and dried.

The solvent used for a polymer to form a membrane depends on the kind of the polymer. Generally, it is to be a good solvent to said polymer and, at the same time, it 35 is to be the one which can be quickly substituted by a

solidifying liquid on immersion. In many cases, water is used as a solidifying liquid. Therefore, it is preferable to use a polar solvent which has a compatibility with water. For example, when a polysulfone is used as a polymer for

5 forming a membrane, dioxane, tetrahydrofuran, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone or a mixture of them are suitable. In the case of using polyacrylonitrile, solvents such as dioxane, N-methyl-2-pyrrolidone, dimethylformamide,
10 dimethylacetamide and dimethylsulfoxide are suitable. Also, dimethylformamide and dimethylacetamide in the case of a polyamide and dichloroethane, acetone, dioxane, tetrahydrofuran or N-methyl-2-methyl-2-pyrrolidone in the case of cellulose acetate are respectively suitable.

15 On the other hand, a preferable non-solvent is a solvent which does not dissolve a polymer and, at the same time, has a sufficient compatibility with a solidifying liquid. Examples of such a non-solvent are water, methanol, isopropanol, polyethylene glycol and glycerin. When such
20 non-solvent is mixed with a good solvent, the amount of the former is not restricted so far as it is within a range where the resultant mixture solution can maintain its homogeneity. However, a preferable amount of the non-solvent is 5 - 50% by weight.

25 Also, in order to control the porous structure, a swelling agent such as an inorganic or organic electrolyte, or a macromolecule or its electrolyte can be added to the polymer solution.

Examples of such a swelling agent are metal salts
30 of inorganic acids such as sodium chloride, sodium nitrate, potassium nitrate, sodium sulfate, or zinc chloride; metal salts of organic acids such as sodium acetate, sodium formate; macromolecules such as polyethylene glycol or poly(vinyl-pyrrolidone), macromolecular electrolytes
35 such as polystyrene sodium sulfonate, poly(vinyl-benzyl-

trimethyl ammonium chloride) and ionic surface active agents such as di-octylsulfo sodium succinate, or an alkyl methyl sodium taurinate. These swelling agents give their effects to some extent even when they are added as they are to a polymer solution. However, when they are added in a form of an aqueous solution, they can exert large effects. Although there is no restriction on the amount of the aqueous swelling agent solution to be added so far as the homogeneity of the polymer solution is maintained, it is usually 0.5 - 10 % by volume to the solvent. As for the concentration of the aqueous swelling agent solution, there is no restriction thereon but ordinarily it is from 1 to 60 % by weight.

The concentration of the polymer solution for forming a membrane is to be 5 - 35 % by weight, preferably 10 - 30 % by weight. If the concentration is higher than 35 % by weight, the water permeability of the obtained micro-porous membrane becomes so low as to be impractical, while the concentration lower than 5 % by weight does not give a membrane having a sufficient filtration ability.

The micro-porous membrane of the present invention can be produced by spreading the raw solution obtained as above over a support, then adjusting the amount of the solvent evaporating from the spread raw solution and the amount of the non-solvent vapor absorbed by it according to various methods.

For example, the raw solution is spread over a support and air having an absolute humidity of more than 2 g H₂O/Kg. Air is blown on the surface of the spread solution at a rate of higher than 0.2 m/sec, whereby a coacervation phase is formed to deeper than 1 μ m, preferably as deep as 1 - 30 μ m below the surface of the spread solution. Then the resulting membrane is immediately immersed in a solidifying bath to form a micro-porous membrane.

The micro-porous membrane obtained in this way has the minimum pore layer at the deepest part of the coacervation. This is different from the membrane obtained by the known method, in which the spread solution is immersed after it is maintained for some time in air or in a non-solvent atmosphere.

In this case, it is preferred that the ratio between the diameter of the pores on the top side of the obtained membrane and that of the other side is from 1 : 10 to 1 : 1000, and the specific surface area measured by the BET method is in a range of 8 - 80 m²/g. If the specific surface area is larger than 80 m²/g, the physical strength of the membrane becomes reduced, therefore the range of the specific surface area of 20 - 60 m²/g is better.

The reason why the micro-porous membrane having the layer of minimum pores inside can be obtained by the present invention is not known clearly. However, it is presumed to be as follows: a layer of minimum pores seems to be formed in between the layer in which said micro-phase separation due to the solvent evaporation and the non-solvent's penetration occurred and that in which no such separation took place. When the membrane is immersed in a solidifying liquid before the diameters of the pores in said layer grow, the layer of minimum pores can be fixed. Then, since the solidifying liquid permeates very slowly through said minimum pore layer to the inner part of the spread solution, the micro-phase separation due to the penetration of the non-solvent proceeds in the part beyond the layer of minimum pores, whereby micro-pores having longer diameters than that of the pores in the minimum pore layer are formed.

In the traditional methods, in order to let pores form in the surface area of a membrane which is used in a field of micro-filtration, the raw solution for forming a membrane is spread over a support after the solution has slightly developed its phase separation, and the spread

solution is immersed in a solidifying liquid (e.g., Japanese Patent Publications (OPI) Nos. 154,051/'81 & 145,740/'83).

However, the weakest point of such methods is that the stability of the raw solution in the state of such phase separation is very poor so that the solution needs to be formed into a membrane within a short period of time after the preparation of the solution in said state, otherwise precipitates are formed in the solution and a further filtration process becomes necessary as disclosed in the bulletin of Japanese Patent Publication (OPI) No. 145,740/'83. On the other hand, if the development of the phase separation is suppressed to secure the stability of the raw solution, a skin layer is formed on the surface of the membrane, which makes it unsuitable as a filter for micro-filtration. The present invention, however, does not suffer from such a problem, since a raw solution is prepared to be a completely homogeneous system, and after it is spread the spread solution is immersed in a solidifying bath when a vapor of a non-solvent (e.g., water) is supplied from the air to let the spread solution absorb it while the solvent in the solution is evaporated to cause a state of phase separation only in the area near the surface.

According to the present invention, both sides of an asymmetric membrane which has not been obtainable so far can be produced by controlling the amount of the non-solvent contained in the gas which is in contact with the surface of the spread solution as well as the blowing rate of the gas toward said surface. In this case, since the phase separation is caused to occur only in the area near the surface, it is necessary to let the non-solvent vapor be absorbed into the spread solution uniformly within a very short time and the solution be solidified immediately. By adjusting this absorption of the non-solvent vapor, it is possible to adjust the depth of the minimum pore layer and the diameter of the pores in it.

In order to make the present invention effective, it is especially necessary to previously add to a raw solution not only a solvent suitable for the polymer used but also a non-solvent and a swelling agent. Examples of
5 such a non-solvent and a swelling agent are polyethylene glycol, poly(vinylpyrrolidone), water, etc. as mentioned before.

The conditions for producing the present micro-porous membrane depend on the kind of the polymer, solvent,
10 non-solvent and swelling agent to be used, the concentration of the polymer, the atmosphere in which the raw solution is spread, etc. It is important to find out the most desirable conditions by studying the timing of the micro-phase separation and the structure of the membrane. The thus
15 obtained conditions can be controlled by adjusting the amount of the solvent evaporating from the spread raw solution and the amount of the non-solvent vapor absorbed by it according to various methods.

Such an adjustment can be accomplished, for
20 example, by adjusting the period of time from spreading of the raw solution to immersion of it in a solidifying bath. This time adjustment is carried out e.g., by covering the course of the polymer solution from the place where it is spread to that of the solidifying bath; or by adjusting
25 the vapor pressures of the good solvent and non-solvent, temperature, rate of aeration, etc. in the atmosphere where the present process is carried out.

The polymer solution removed from the solidifying liquid has acquired a self-supporting ability. Thus, it is
30 peeled off from the support used for reinforcement and immersed in a rinsing bath. After rinsing the membrane with water, it is dried and either rolled up or further treated to make it hydrophilic.

EXAMPLES

While the present invention is further explained in detail by reference to examples thereof, it is not to be restricted by them. The unit, "part", used to express amounts added means "part by weight".

EXAMPLE 1

A homogeneous raw solution for forming a membrane was prepared by dissolving 20 parts of polyvinylidene fluoride (KYNAR ®: manufactured by Pennwalt Co., Ltd. U.S.A.), 60 parts of dimethylacetamide as a good solvent, and a non-solvent consisting of 10 parts of polyethylene glycol 200, 10 parts of poly(vinylpyrrolidone) and 0.7 parts of water. The obtained solution was spread evenly over a glass plate using a doctor blade so as to have a spread solution thickness of 150 μ m, and warm air at 60 °C (relative humidity: 30 %) was blown on to the surface of the spread solution samples at a rate of 0.8 m/sec for 0, 2, 6, 10 & 30 seconds, respectively. Then, the samples were immediately immersed in warm water at 60 °C for 2 minutes and further in water at 20 °C to obtain micro-porous membranes. The structure of each membrane was examined by an electron microscope. The results are shown in Table 1.

It is apparent from the above results that the minimum pore layer was formed inside the membrane when warm air was blown for 2 to 10 seconds.

Example 2

A raw solution for forming a membrane was prepared by homogeneously dissolving 15 parts of polysulfone (P-3500 manufactured by U.C.C. Co.), in 70 parts of N-methyl-2-pyrrolidone, 15 parts of poly(vinylpyrrolidone) and 0.8 parts of water. The solution was let flow to spread over a glass plate with a casting coater so as to have a spread solution thickness of 150 μ m, and warm air at 40 °C (relative humidity: 60 %) was blown on to the surface of the spread solution samples at a rate of 2 m/sec for 2, 4, 6,

Table 1.

Period of Time for Blowing	Diameter of the Pores on the	Depth from the		Diameter of the Pores on the	Thickness of the Membrane
		Surface to the Minimum	Pore Layer		
<u>Warm Air</u>		<u>Surface</u>	<u>Back Side</u>		
0 sec.	0.05 μ m	Surface	1 μ m	100 μ m	
2 "	0.08 "	2 μ m	2.5 "	114 "	
6 "	0.15 "	10 "	10 "	103 "	
10 "	0.80 "	25 "	10 "	115 "	
30 "	1.2 "	not clear	20 "	110 "	

10, 20 & 30 seconds, respectively. The samples were immediately immersed in a solidifying bath containing water at 20 °C to obtain micro-porous membranes. The membranes which had a minimum pore layer inside them were those blown with the above air for 2 to 20 seconds. The one blown for 30 seconds did not have such a layer clearly.

From the electron microscopic photograph of the section of the membrane (Fig. 1) which was left to stand in the air for 4 seconds, a fine layer of which micro-pore diameters were shorter than those of the pores on the membrane surface was found to be at the depth of about 10 μm below the surface.

The amount of permeated water and the ability to remove polystyrene latex particles were examined using the present invention's membrane prepared by aeration for 4 seconds (average diameter of the minimum pores: 0.2 μm), a marketed Membrane A for comparison which is an asymmetric membrane and has minimum pores in its surface layer (made of polysulfone, average diameter of the minimum pores: 0.2 μm), and a marketed symmetrical Membrane B (made of polyvinylidene fluoride, average diameter: 0.2 μm).

The ability to remove the particles was evaluated by filtering polystyrene latex (manufactured by Dow Corning Co., Ltd.) having an average particle diameter of 0.236 μm in an amount of 10^6 particles per 1 cm^2 of the filtration area of each membrane, and by counting the number of particles which passed through the membrane.

For comparison, two of the marketed Membranes A were put together so as to let their minimum pore layers contact each other, the combination being designated "Membrane A'" (according to the method described in Japanese Patent Application (OPI) No. 150,402/'83). The ability of this membrane to remove particles was also examined. The results are in Table 2.

Table 2

	The membrane of the present invention	Membrane A	Membrane B	Membrane A'
Amount of water permeated (ml / cm ² / min / atm)	45	30	15	—
Number of the particles which passed through the membrane	3	about 2,000	about 30,000	40

10

As is apparent from the above Table 2, the membrane of the present invention has a low filtration resistance, whereby in spite of a large amount of permeated water the number of the particles which passed through the film was small (greater ability to remove the particles). Thus, the membrane is highly effective.

Although Membrane A' which was made of two membranes as above has an improved ability to remove particles compared with that of Membrane A, it is not as excellent as the present invention's membrane which was, as a result, proved to be highly reliable.

Example 3

A membrane-forming solution comprising 15 parts of polysulfone ("P-3500" produced by Union Carbide Coop. Ltd.), 60 parts of N-methylpyrrolidone, 15 parts of polyethyleneglycol, 5 parts of poly(vinylpyrrolidone) and 5 parts of LiCl was let flow to spread over a glass plate to have a thickness of 150 μ m and was exposed to the air having a relative humidity of 40 %, a temperature of 25 $^{\circ}$ C at an aeration rate of 0.7 m/sec for 15 seconds. After the coacervation phase was formed on the surface, the layer on the plate was immersed in water at 25 $^{\circ}$ C for solidification to obtain a micro-porous membrane. The pore diameter of the top side of this membrane was from 0.5 to 1 μ m, while that of the other side was from 1 to 10 μ m. The average diameter of the pores

in the minimum pore layer was $0.15\mu\text{m}$, and the specific surface area was $41\text{ m}^2/\text{g}$. It was confirmed by an observation of the membrane section with an electron microscope that the minimum pore layer existed within the membrane itself.

5 Fig. 2 shows the relation between depth from the top surface to the minimum pore layer and the specific surface area obtained by varying the aeration time. It is apparent from the figure that the deeper the place of the minimum pore layer within the membrane, the greater the specific
10 surface area.

Comparative Example

The solution in Example 3 was let flow to spread over a glass plate to have a thickness of $150\mu\text{m}$ and immediately immersed in water at 25°C to obtain a micro-porous membrane.
15 The average pore diameter of the top side of this membrane was $0.15\mu\text{m}$, while the diameter of the other side was from 10 to $100\mu\text{m}$. The specific surface area was $5\text{ m}^2/\text{g}$. An electron microscopic photo of the membrane section showed that the minimum pore layer existed in the topmost surface
20 of the membrane.

Example 4

Filtration tests were carried out with respect to the present invention's membrane obtained in Example 3 and the membrane obtained in the comparative example.

25 An aqueous solution containing 0.01 wt% of polystyrene latex (average particle size: $0.17\mu\text{m}$) was subjected to the filtration tests using the two membranes with a pressure difference between pressures before and behind the membrane of 0.1 kg. As a result, the membrane obtained in the
30 comparative example substantially got blocked after filtering $500\text{ ml}/\text{cm}^2$ of the solution, while the membrane of the present invention was able to filter $1,200\text{ ml}/\text{cm}^2$ of the same. Thus, it was proved that the present invention's membrane had a greatly improved filtration life.

CLAIMS:

1. A micro-porous membrane having a distribution of pore diameters in the direction of thickness thereof, which contains a layer of minimum pores inside the membrane
5 itself.

2. A micro-porous membrane as claimed in Claim 1, wherein said layer of minimum pores exist at a depth of 1 - 30 μm below the surface thereof.

3. A micro-porous membrane as claimed in Claim 1
10 or Claim 2, wherein said membrane is made of a polysulfone or polyether sulfone.

4. A micro-porous membrane as claimed in any preceding claim, wherein the ratio between the diameter of the pores on the top side of the membrane and that of the other side
15 is from 1 : 10 to 1 : 1,000.

5. A micro-porous membrane as claimed in any preceding claim, wherein the specific surface area is larger than 8 square meters per gram.

6. A micro-porous membrane as claimed in Claim 5,
20 wherein said specific surface area is from $8 \text{ m}^2/\text{g}$ to $80 \text{ m}^2/\text{g}$.

7. A micro-porous membrane as claimed in Claim 1 substantially as hereinbefore described with reference to Example 1, 2 or 3.

8. A micro-porous membrane as claimed in Claim 1,
25 having a structure substantially as shown in Fig. 1 of the accompanying drawing.

9. A process for producing a micro-porous membrane, wherein (a) a polymer solution is prepared by dissolving a polymer for forming a membrane in a mixture of a good
30 solvent for said polymer and optionally a non-solvent for the same, (b) the solution is spread over a support, (c) a phase separation is caused on the surface of the spread solution to obtain a micro-porous membrane having a layer of minimum pores inside, and (d) the membrane is immersed
35 in a solidifying liquid to form a micro-porous membrane.

10. A process for producing a micro-porous membrane as claimed in Claim 9, wherein water is used as a solidifying liquid and a polar solvent compatible with water

is used as a good solvent for said polymer.

11. A process for producing a micro-porous membrane as claimed in Claim 10, wherein air having an absolute humidity higher than 2 grams H_2O/Kg air is blown on to the surface of the membrane of said polymer solution at a rate of higher than 0.2 m/sec.

12. A process for producing a micro-porous membrane as claimed in Claim 9, 10 or 11, wherein the ratio of the good solvent and the non-solvent is from 95 : 5 to 50: 50.

13. A process as claimed in Claims 9, 10, 11 or 12, wherein the concentration of the polymer solution is from 5 to 35 weight per cent.

14. A process as claimed in any of Claims 9 to 13, wherein the polymer solution contains a swelling agent.

15. A process for producing a micro-porous membrane as claimed in Claim 14, wherein said swelling agent is added by adding a solution containing 1 - 60 wt% of the swelling agent in an amount of 0.5 - 10 volume % based on the amount of good solvent and any non-solvent in the polymer solution.

16. A process for producing a micro-porous membrane as claimed in Claim 9, substantially as hereinbefore described with reference to Example 1, 2 or 3.

17. A process as claimed in any of Claims 9 to 16, wherein a membrane as claimed in any Claims 1 to 6 is produced.

18. A membrane as claimed in any of Claims 1 to 8 or produced by the process of any of Claims 9 to 16, when used for the filtration of small particles.

